

PATENT  
Docket No. 30-4012

## NO<sub>x</sub> REMOVAL APPARATUS INCLUDING MANGANESE DIOXIDE AND COPPER OXIDE SUPPORT

This application claims the benefit of provisional application no. 60/066,146 filed  
5 on November 19, 1997.

### BACKGROUND OF THE INVENTION

The present invention relates to NO<sub>x</sub> removal. More specifically, the invention relates to an adsorbent for removing nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) from a  
10 gas such as air.

NO<sub>x</sub> removal systems are commonly used in applications ranging from air filtration to auto emission control. U.S. Patent No. 5,362,463 discloses a NO<sub>x</sub> adsorbent including a support made of a mixture of manganese oxide and aluminum oxide. Between 20 percent and 80 percent manganese oxide is used, with the remainder being aluminum oxide. The adsorbent further includes an alkali material such as potassium carbonate. The '463 patent discloses that potassium is used in amounts ranging between five and fifty percent. As air flows over the adsorbent, NO<sub>x</sub> is removed.

20 NO<sub>x</sub> removal is performed at high air temperatures. ~~The air temperature exceeds 200°C.~~ According to the '463 patent, there are temperature limitations on the removal of the NO<sub>x</sub> at air temperatures below 100°C.

It would be desirable to remove NO<sub>x</sub> at temperatures below 100°C.

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### SUMMARY OF THE INVENTION

NO<sub>x</sub> is removed at lower temperatures by an apparatus according to the present invention. The apparatus includes a support made of a mixture including manganese dioxide and copper oxide; and an alkali material combined with the support. The support and the alkali material are combined for NO<sub>x</sub> removal. The apparatus can  
30 remove NO<sub>x</sub> from a gas such as air at temperatures below 100°C. The apparatus has a high NO<sub>x</sub> removal capacity, and it is durable to air and thermal exposure.

According to different aspects of the invention, the support may be impregnated with the alkali material, the support and the alkali material may be formed as separate particles that are mixed together, or the support and the alkali material may be formed as separate particles that are placed in separate vessels.

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**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is an illustration of a NOx removal system according to the present invention;

10 Figure 2 is an illustration of a method of forming an adsorbent for the NOx removal system according to the present invention; and

15 Figure 3 is an illustration of an alternative NOx removal system according to the present invention.

**DETAILED DESCRIPTION OF THE INVENTION**

Figure 1 shows a NOx removal system 10 including a vessel 12 containing an adsorbent 14. The vessel 12 is contained within an enclosure 16. During NOx removal, an incoming stream 18 of gas such as air is flowed over the adsorbent 14. The adsorbent 14 reduces the levels of nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) in the gas. Leaving the vessel 12 is a stream 20 of gas having reduced levels of nitric oxide and nitrogen dioxide.

20 The adsorbent 14 can remove the NOx in gas having a temperature above 100°C. However, the adsorbent 14 can also remove NOx in gas having a temperature below 100°C. The adsorbent 14 can even remove NOx in a gas having a temperature of 35°C or perhaps lower than 20°C. Thus, the adsorbent 14 can remove NOx at low temperatures.

25 The incoming gas 18 may be heated or cooled to a temperature at which NOx removal occurs (the "operating" temperature). If, however, the gas is already at a desirable operating temperature, then a separate heater or cooler is not used. For example, the enclosure 16 is a vehicle including a combustion engine, and it is desired

a to remove NO<sub>x</sub> in exhaust gas from the combustion engine. The exhaust gas from the combustion engine is already heated. *Therefore*, the exhaust gas from the combustion engine could be flowed directly over the adsorbent 14.

5 The adsorbent 14 includes two components: an alkali material, and a support for the alkali material. The support is a mixture including manganese dioxide (MnO<sub>2</sub>) and copper oxide (CuO). At least about sixty weight percent (60 wt%) manganese dioxide is included in the mixture, and at least about ten weight percent (10 wt%) copper oxide is included in the mixture. The support may be made of commercially available mixtures such as "CARULITE 200" (available from Carus Chemical Co. located in Peru, Illinois) 10 and "HOPCALITE" (available from Strem Chemicals located in Newburyport, Massachusetts). The "CARULITE 200" mixture includes about sixty to seventy five weight percent manganese dioxide (60 wt% to 75 wt% MnO<sub>2</sub>), about eleven to fourteen weight percent copper oxide (11 wt% to 14 wt% CuO), and about fifteen to sixteen weight percent aluminum oxide (15 wt% to 16 wt% Al<sub>2</sub>O<sub>3</sub>). The "HOPCALITE" mixture includes at least seventy weight percent manganese dioxide (70 wt% MnO<sub>2</sub>) and at least ten percent copper oxide (10 wt% CuO). No aluminum oxide is believed to be present. In addition to supporting the alkali material, the support performs a function of oxidizing the nitric oxide into nitrogen dioxide.

20 The support mixture may be formed as particles that are porous. The porous support particles may have a high internal surface area of at least 150 meters<sup>2</sup>/gram. The geometry of the support particles may be pellets, granules, cylinders, spheres, extrudates, powders, etc. The support particles may have a size as large as five (5) millimeters. It has been found that smaller particles exhibit better gas diffusion and removal efficiency than larger particles.

25 The alkali material may be potassium carbonate (K<sub>2</sub>CO<sub>3</sub>). The alkali material removes the nitrogen dioxide by a chemical reaction, which generates nitrate and/or nitrite on the adsorbent's exposed surface. The adsorbent 14 includes about three to forty weight percent potassium carbonate (3 wt% to 40 wt% K<sub>2</sub>CO<sub>3</sub>), with the remainder being the support.

The alkali material may instead be potassium hydroxide (KOH) or another alkali or alkaline-earth carbonate or hydroxide. For example, carbonates of calcium (Ca), lithium (Li), sodium (Na), rhubidium (Rb), or cesium (Cs) may be used.

Separate tests have been conducted on adsorbents 14 including "CARULITE 200" particles and "HOPCALITE" particles, and it has been found that both adsorbents work well on air having temperatures between 21°C and 450°C. Efficiency of the NO<sub>x</sub> removal increases as the temperature is increased. This temperature dependence is more pronounced with the nitric oxide than with the nitrogen dioxide.

Optimal loading of the potassium carbonate has been found to vary in proportion to the operating temperature of the gas. For an operating temperature of 50°C, an optimal loading of potassium carbonate has been found to be in the range of three weight percent to twelve weight percent (3 wt% to 12 wt% K<sub>2</sub>CO<sub>3</sub>), and preferably ten weight percent (10 wt%). For an operating temperature of 250°C, an optimal loading of potassium carbonate has been found to be between twenty weight percent and forty weight percent (20 wt% and 40 wt% K<sub>2</sub>CO<sub>3</sub>), and preferably thirty weight percent (30 wt%). For temperatures between 50°C and 250°C, the weight percent of the potassium carbonate could be interpolated.

The alkali material may be combined with the support in different ways. For example, inert support particles could be coated with the alkali material, and the coated inert particles could be uniformly dispersed in the vessel 12 with the support particles (e.g., the "CARULITE 200" particles or "HOPCALITE" particles). The inert particles for the alkali material could be high surface area alumina particles as well as particles such as silica, titania and zirconia. The inert particles also have a high internal surface area for dispersion of the alkali material. The surface area may be above about 10 meters<sup>2</sup>/gram.

In the alternative, the support and alkali may be layered within the vessel 12. For example, the support particles may be placed in front of inert particles that are coated with alkali material.

Figure 2 illustrates yet another way in which the support and alkali material may be combined. The support particles (e.g., the "CARULITE 200" particles or "HOPCALITE" particles) may instead be coated or impregnated with the alkali material.

The support particles may be procured from a commercial manufacturer or produced by mixing together the manganese dioxide and copper oxide (block 100). The support particles may be produced by starting with a mixture of water soluble salts of manganese and copper, followed by precipitation and calcining.

5 An additional material such as chromium oxide may optionally be added to the support mixture (block 102). The chromium oxide may be added, for example, by impregnating the support mixture with water soluble chromium salt, or mixing the water soluble chromium salt with the water soluble salts of manganese and copper.

10 The support particles may then be impregnated with the alkali material by forming an aqueous solution of the alkali material (block 104), impregnating the support particles with the aqueous solution (block 106), and drying the impregnated support particles (block 108). Impregnating the support particles with the aqueous solution allows direct physical contact between the support particles and the alkali material because the alkali material is deposited on the support particles.

15 After being dried, the impregnated support particles may also be heat treated at a temperature above the expected operating temperature of the gas (block 110). If, however, the impregnated particles are dried at a temperature above the expected operating temperature of the air, the heat treatment step (block 110) may be skipped.

20 Such an absorbent may be formed, for example, by combining 10 wt% potassium carbonate ( $K_2CO_3$ ) with "CARULITE 200" particles. These two components are combined by impregnating 100 grams of commercially available "CARULITE 200" particles with 70 mL of an aqueous solution of  $K_2CO_3$  containing 11 grams of  $K_2CO_3$ .  
25 The impregnated support particles are then dried in a rotary impregnator at a temperature of 100°C. Both the "CARULITE 200" particles (prior to impregnation) and the dried particles (after impregnation) are sieved to 20-35 Tyler mesh.

Figure 3 shows yet another way in which the support and alkali material may be combined. A first vessel 200 containing the support 202 (e.g., "CARULITE 200" particles) is followed by a second vessel 204 containing the alkali material on inert particles 206. During NOx removal, a stream 208 of gas is passed over the support 202 in the first vessel 200. A gas stream 210 leaving the first vessel 200 bed is then passed

over the alkali material in the second vessel 204. A gas stream 212 leaving the second vessel 204 has reduced levels of nitric oxide and nitrogen dioxide.

Still another way of combining the support and alkali would be to place the support 202 in the first vessel 200 and the alkali-coated support 14 in the second  
5 vessel 204.

Thus disclosed is an adsorbent that can remove NOx in a gas having a temperature below 100°C. The adsorbent can reduce the problems associated with raising the temperature of the gas prior to NOx removal. In certain instances, the adsorbent might allow a heater to be eliminated. In other instances, the adsorbent  
10 might be placed in a more convenient location inside the enclosure. For example, if the gas stream temperature varies at different locations within the enclosure, the invention  
15 will afford greater flexibility in placing the adsorbent along the gas stream, especially if the gas stream temperature is below 100°C at certain locations.

The adsorbent has been found to exhibit high air exposure and thermal  
15 durability. Resulting is an adsorbent having a long lifetime.

The adsorbent is also believed to have a higher NOx adsorption capacity. The higher adsorption capacity allows the adsorbent to be used for longer periods before the adsorbent becomes saturated. After the adsorbent becomes saturated, it could be discarded. In the alternative, the adsorbent could be regenerated. Still, the longer  
20 lifetime of the adsorbent would reduce the frequency of regeneration.

The invention may be used, without limitation, for the removal of NOx from breathable air; the removal of NOx from combustion engine exhaust; the removal of NOx from gas streams generated by coal and residual oil burning furnaces; the removal of NOx from catalytic oxidizers and non-catalytic thermal oxidizers that process  
25 nitrogen-containing organic molecules such as amines; the removal of NOx from nitric acid production plants; and the removal of NOx from nitrite production plants. During the NOx removal, oxygen should be present.

Design considerations such as adsorbent size, gas flow rate, and desired NOx levels in the effluent gas will depend upon the application for which the NOx removal  
30 system is intended.

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The present invention is not limited to the specific embodiments described above. Instead, the present invention is construed according to the claims that follow.